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(54) Title: RAPID MANUFACTURING OF CARBON NANOTUBE COMPOSITE STRUCTURES

(57) Abstract: A system for fabricating a free form structure of a composite material including carbon nanotubes. The system includes a discharge assembly and a composite formation device operatively linked with the discharge assembly. The discharge assembly dispenses a fusing agent such as for example a high energy density emission, a laser emission or a particle beam emission. The composite formation device includes a composite generator and an arranger in operative engagement with a composite generator. The composite generator engages with the fusing agent so as to create a composite nodal element. The composite nodal element includes a matrix and a multiplicity of fibers formed of carbon nanotubes dispersed throughout the matrix. The arranger positions one node relative to another to define the free form structure.

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## RAPID MANUFACTURING OF CARBON NANOTUBE COMPOSITE STRUCTURES

### BACKGROUND OF THE INVENTION

This application claims priority of U.S. Provisional Application Serial No. 60/245,916, filed November 3, 2000, entitled "Carbon Nanotube and Metal/Ceramic/Polymer Matrix Composites Produced Through Direct Manufacturing and Netshaped Manufacturing Methods," and U.S. Utility Application Serial No. 90/xxx,xxx, filed October 24, 2001 entitled "Rapid Manufacturing of Carbon Nanotube Composite Structures," which are incorporated herein by reference in their entirety.

The present invention generally relates to the creation of free-form composite structures with rapid manufacturing techniques. More particularly, the invention relates to a system and method for fabricating a free-form structure by arranging one composite nodal element relative to another. More particularly, it further relates to generating a composite nodal element containing a matrix and a multiplicity of discrete fibers formed of carbon nanotubes dispersed throughout the matrix.

Three common allotropes of carbon are diamonds, graphite and fullerenes, such as the Buckyball. For example, carbon nanotubes are a type of fullerene that exhibit mechanical strength and strain characteristics greater than steel and other alloys but exhibit low density characteristics similar to or below that of current ceramic or polymer composites.

Because of their low density, carbon nanotube composites are often difficult to produce when combined with a denser metal, ceramic or polymer matrix. Frequently, during the formation of such composites, gravity pulls and, ultimately, separates denser composite materials from that of the lightweight carbon nanotube composite material. Moreover, due to their electrostatic characteristics, carbon nanotubes tend to conglomerate with one another during the composite formation process rather than homogeneously dispersing with matrix composite materials.

The tendency for the non-homogeneous formation of carbon nanotubes within a composite matrix often results in the application of a non-optimal composite for use by a host system. Accordingly, subjecting such non-optimized composite components to various physical factors over time can result in fractures, fatigue, wear, and possibly,

catastrophic failure of that component. Furthermore, the application of post-processing procedures to non-optimized carbon nanotube composites also increases the possibility of a catastrophic failure. For example, machining and other finishing processes impose unnecessary forces and conditions on such composites that can possibly damage the overall matrix arrangement.

Although composites that include carbon nanotubes homogenously dispersed throughout a metal/ceramic/polymer matrix possess certain technical advantages, including favorable physical properties among others, methods for producing these composites have serious limitations. As such, it is very difficult, costly, and time consuming to create a composite where carbon nanotubes are homogeneously dispersed throughout a matrix. For example, manufacturing processes often include a two-step routine of initially forming a composite material and then processing the material so as to define a structure for use with a host system.

Many conventional composite formation techniques fail to meet the requirements for producing carbon nanotubes homogeneously dispersed throughout a metal/ceramic/polymer matrix. Present manufacturing techniques typically form these composites by applying heat and pressure. Unfortunately, the improper application of either heat or pressure often diminishes the net yield of carbon nanotubes formed within the matrix. As such, current composite manufacturing techniques suffer from the limitation of decreasing the yield of carbon nanotubes formed within a matrix due to the improper application of either heat or pressure.

Moreover, in addition to the non-homogeneous dispersment of carbon nanotubes, typical composite formation processes do not randomly align carbon nanotubes throughout a matrix apart from their crystalline and electrical characteristic tendency to conglomerate with one another. This lack of random alignment fails to mitigate or eliminate the propagation of crack formations within a matrix due to the repetitive application of physical forces over time.

In addition to composite manufacturing techniques, current finishing processes for ultimately forming a component part further subject composite material to heat and pressure that can further diminish the effective amount of carbon nanotubes within a matrix. Accordingly, there currently does not exist an apparatus and method for

forming a resulting composite component part having an optimal and homogeneous yield of carbon nanotubes within a matrix and without the added step of processing the composite material to form a component part.

### BRIEF SUMMARY OF THE INVENTION

5 In accordance with the present invention, a free-form structure is generated so that carbon nanotubes are controllably dispersed throughout a matrix composite with little or no need for post-processing procedures so as to optimize the yield of carbon nanotubes within the matrix. Accordingly, *via* a system implementing rapid manufacturing techniques, carbon nanotubes are randomly as well as homogeneously  
10 dispersed as a single stream of powdered-gas mixture for combination with a fusing agent. The resulting composite enjoys an optimal yield of carbon nanotubes homogeneously and randomly dispersed with the matrix. In one exemplary embodiment, the carbon nanotubes are a fiber of a predetermined length designed to blunt a crack formation and, thus, failure of a composite material when subjected to  
15 fatigue. In effect, randomly aligned, discrete carbon nanotube fibers inhibit the propagation of crack formation in a broad range of directions so as to improve the loading ability of a resulting composite in a variety of directions.

According to one embodiment of the present invention, a system for fabricating a free-form structure includes a discharge assembly and a composite formation device  
20 operatively linked with the discharge assembly. The discharge assembly dispensing a fusing agent such as a high-energy density emission, a laser emission or particle beam emission for example. The composite formation device includes a composite generator and an arranger in operative engagement with the composite generator. Ultimately, the composite generator engages with the fusing agent so as to create a composite nodal  
25 element.

The composite nodal element includes a matrix and a multiplicity of fibers formed of carbon nanotubes dispersed throughout the matrix. One exemplary embodiment, for a composite nodal element, a multiplicity of discrete fibers formed of carbon nanotubes range in length from about 10 nanometers to about 500 microns. The  
30 arranger positions one node relative to another to define the free-form structure.

A technical advantage of the present invention provides for the nodes containing carbon nanotubes that are arranged with respect to each other, illustratively in a similar manner to that of building blocks, to define a free-form structure without the need of a mold or machining or other post-processing operations. The system, based on a template, controls the size, dimensioning, tolerancing, and material make-up of the resulting free-form structure as it deposits and arranges the multiplicity of composite nodal elements. In one exemplary embodiment, the fibers formed of carbon nanotubes comprise reinforcement fibers for strengthening the matrix and overall free-form structure illustratively in a similar manner to that of reinforced concrete. It should be also added that in one exemplary embodiment, the matrix includes a metal. Moreover, in one exemplary embodiment, the matrix includes a metal alloy. In another exemplary embodiment, the matrix includes an intermetallic compound. In another exemplary embodiment, the matrix includes a ceramic. In another exemplary embodiment, the matrix includes a polymer. Those of ordinary skill in the art will readily recognize any combination of matrix materials for combination with the carbon nanotube fibers.

Another technical advantage includes a program executed through a computer-readable code for fabricating a free-form structure with a fabrication system. The program includes a composite formation program code and a structure formation program code. The composite formation program code generates a composite node *via* a composite generator by combining a matrix and a multiplicity of fibers formed of carbon nanotubes with a fusing agent. The structure formation program code arranges one composite node relative to another *via* the arranger to define a free-form structure.

In one exemplary embodiment, the arranger includes a positioning assembly. The positioning assembly moves each one of the nodes according to instructions based on a computer-readable code. The positioning assembly in one exemplary embodiment stores a template associated with the free-form structure.

Accordingly, one technical advantage of the present invention includes the positioning assembly arranging each one of the nodes according to the template.

Moreover, one technical advantage of the present invention provides a system and method for homogeneous formation of carbon nanotubes within a matrix composite.

One technical advantage of the present invention includes a control system for forming the carbon nanotube composite and for arranging the composite into a desired free-form structure.

One technical advantage includes the control system mapping out to scale a  
5 resulting component part based on a pre-existing CAD file for that part.

One technical advantage of the present invention includes a fusing agent, such as a laser, for combining carbon nanotubes with other powdered materials so as to form a node or "bead" defined by the desired homogeneous composite material.

One technical advantage of the present invention includes a system for  
10 constructing a free-form structure node-by-node so that the resulting structure is to scale with minimal or no need for post-production processing, such as machining or the use of a pre-form/mold.

Other aspects, advantages and novel features of the present invention will become apparent from the detailed description of the invention when considered in  
15 conjunction with the accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS:

For a more complete understanding of the present invention and advantages thereof, reference is now made to the following description which is to be taken in conjunction with the accompanying drawings and which like reference numerals  
20 indicate like features and wherein:

FIG. 1 is a schematic diagram illustrating material formation of a composite nodal element by combining a matrix and a multiplicity of discrete fibers formed of carbon nanotubes;

FIG. 2 is a schematic diagram illustrating a system according to the present  
25 invention for fabricating a free form structure by positioning one composite nodal element relative to another;

FIG. 3 is a schematic diagram illustrating another embodiment of a system for fabricating a free-form structure;

FIG. 4 is a perspective view illustrating the system of Figure 3 featuring the  
30 generation of a free-form structure through the deposition of one composite nodal element relative to another.

FIG. 5 is an isometric view illustrating the formation of a composite nodal element containing a multiplicity of discrete fibers formed of carbon nanotubes dispersed throughout a matrix such that a free-form structure is defined by positioning the composite nodal element relative to another;

5        FIG. 6 is a schematic diagram illustrating another embodiment of a system for fabricating a free-form structure;

FIG. 7 is a flow diagram illustrating a free-form fabrication sequence implemented by a system of the present invention; and

10        FIG. 8 is a flow diagram illustrating a composite nodal element formation sequence implemented by a system of the present invention.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Preferred embodiments of the present invention are illustrated in the Figures, like numerals being used to refer to like and corresponding parts of the various drawings. Figure 1 illustrates one aspect, among others, of a process 5 for combining  
15        carbon nanotubes 7 with a matrix 9 to produce a composite 12. In another aspect of the present invention shown in Figure 5, by discretely forming the composite 12 into composite nodal elements 89, a free-form structure 99 is created, *via* the process 5, by arranging one composite nodal element 89 with respect to another. In effect, composite nodal elements act as "building blocks" that define a free-form structure.

20        In one exemplary embodiment, as shown in Figure 1, carbon nanotube fibers 8 are dispersed between a matrix material 10 provided by the matrix 9 to reinforce the overall free-form structure. By analogizing with reinforced concrete, for example, the carbon nanotube fibers 8 are analogous to reinforcing materials such as steel whereas the matrix material 10 is analogous to that of aggregate or cement. In the continuing  
25        analogy, a composite nodal element 89 of the present invention is analogous to a building block formed of reinforced concrete material so that various building blocks are arranged relative to one another to ultimately define a structure.

Accordingly, constructing and arranging composite nodal elements to define a structure circumvents the common practice in the industry of post-fabrication  
30        processing operations. Initially, a structure is often fabricated in a mold or by machining and then subjected to post-fabrication processing operations. Post-

fabrication processing operations refer to added steps required beyond initial fabrication so that the structure exhibits desired dimensions and tolerancing. Typically, post-processing operations include for example, among others, machining, cleaning, polishing, grinding, deburring, and hole drilling so as to achieve desired dimensions and tolerancing of a fabricated structure.

On the other hand, free form structures in this description and appended claims refers to a structure fabricated in a single operational step that includes requisite dimensioning and tolerancing characteristics. Thus, free form structures are created without a mold or conventional machining techniques, such as for example with a lathe, milling machine so that the object is formed to predetermined dimensioning and tolerancing characteristics. Often, at a great savings of cost, time, labor, and the need for added equipment and maintenance thereof, free-form structures require minimal or no post-fabrication processing such as for example machining or polishing. It should be added that processes associated with fabricating free-form structures are referred to in this disclosure and appended claims as rapid manufacturing systems.

Referring to Figure 1, the carbon nanotube fibers 8 are configured in one exemplary embodiment to exhibit a discrete length-to-diameter ratio. In one exemplary embodiment, the multiplicity of discrete carbon nanotube fibers 7 range in length between about 10 nanometers to about 500 microns. Accordingly, an optimal length-to-diameter provides for homogeneous dispersment of carbon nanotube fibers 8 throughout the matrix 9 as well as provides for the optimal length of carbon nanotube fibers or the formation of a composite nodal element *via* rapid fabrication techniques.

For the matrix 9, it should also be said that the matrix material 10 in one embodiment includes a metal, such as for example titanium. In one exemplary embodiment the matrix material 10 includes a metal alloy such as Ti-6Al-4V. In one exemplary embodiment, the matrix material 10 includes an intermetallic compound such as gamma TiAl. In one exemplary embodiment, the matrix material 10 includes a ceramic such as  $Al_2O_3$ . In one exemplary embodiment, the matrix material 10 includes a polymer such as polyvinyl chloride. Moreover, those of ordinary skill in the art will readily recognize any suitable matrix material for receiving carbon nanotubes for dispersment therein.



Figure 2 schematically shows one exemplary embodiment of a system 15 for fabricating a free-form structure 28. In operation, the system 15 fabricates the structure 28 by arranging one composite nodal element with respect to another. In addition to arranging each nodal element, the system 15 initially forms each composite nodal element from a multiplicity of fibers formed of carbon nanotubes dispersed throughout a matrix.

Accordingly, for the embodiment of Figure 2, the system 15 includes a nanotube dispensing assembly 18 and a matrix dispensing assembly 19. The system further includes a discharge assembly 20 for dispensing a fusing agent therefrom.

Illustratively, in one exemplary embodiment, the discharge assembly 20 comprises a high-powered laser for emitting a fusing agent comprising a high-energy density laser beam emission therefrom. In another exemplary embodiment, the discharge assembly 20 comprises a particle beam device for emitting a fusing agent comprising a particle beam.

Through the application of a fusing agent by the system 15, a composite nodal element is formed by combining carbon nanotubes from the nanotube dispensing assembly 18 and matrix material from the matrix dispensing assembly 19. The system 15 repeats the process for creating a composite nodal element so as to ultimately form the structure 28, node-by-node.

To arrange each composite nodal element, the system 15 further includes an arranger for positioning one node relative to another to define the free-form structure 21. The arranger includes a positioning assembly 22 and a motion controller 21 operatively coupled to the positioning assembly 22. The positioning assembly 22 includes a formation program code 24. The formation program code 24 contains instructions in a computer readable format for the size dimensioning, tolerancing, and material composition of the ultimate free-form structure 28. In one embodiment, the formation program code 24 includes a Computer Aided Design (CAD) file associated with a free-form structure for providing instructions for arranging each composite nodal element according to a desired sizing dimensioning tolerancing and material composition characteristics, among others, required for fabricating that free form

structure. In one exemplary embodiment, the positioning assembly 22 stores a template associated with the free-form structure 28 *via* the formation program code 24.

The positioning assembly 22 includes a structure formation program code 25 for arranging a plurality of elemental nodal elements with respect to instructions for  
5 generating the free-form structure 28. In one exemplary embodiment, the structure formation program code 25 arranges the plurality of elemental nodal elements along a plane or, commonly, a "slice" defining the desired free-form structure 28. The motion controller 21 operatively coupled with the positioning assembly 22 moves the free-form structure 28 during construction thereof for arranging each one of the nodes based on  
10 instructions received from the positioning assembly 22.

Referring to the embodiment of Figure 3, a free-form structure 49 is fabricated *via* a system 30. In one exemplary embodiment, the discharge assembly 43 includes a high energy density heat source. The system 30 includes a discharge assembly 43 for dispensing a fusing agent. Illustrating, examples of a discharge assembly include,  
15 among others, an election beam device, a chemical vapor deposition system, a thermal spray device, a plasma deposition devise, and a molecular beam epitaxi system.

Illustratively, in one exemplary embodiment, the discharge assembly 43 includes a high-powered laser, such as for example a 700 watt neodymium yttrium-aluminum-garnet (Nd:YAG) laser. Accordingly, the high-powered laser emits a fusing agent  
20 comprising a high-energy density laser emission therefrom. In one exemplary embodiment, the fusing agent is transferred from the discharge assembly 43 toward the free-form structure 49 *via* fiber optic cable coupled with the high-powered laser 43 as shown in Figure 3.

The system 30 further includes a composite formation device 35 operatively  
25 coupled with the discharge assembly 43. The composite formation device 35 includes a composite generator for engaging with the fusing agent so as to create a composite nodal element. A composite nodal element contains a matrix and a multiplicity of discrete fibers formed of carbon nanotubes dispersed throughout the matrix. For the exemplary embodiment of Figure 3, the composite generator includes a generation  
30 coupling head 40 isolated from an external environment *via* a processing chamber 37.

The processing chamber 37 encloses the generation coupling head 40 within a formation environment 45.

For one embodiment shown in Figure 3, the generation coupling head 40 receives a fusing agent from the high-powered laser and material from a powder feeder  
5 dispenser 44. In particular, for one exemplary embodiment, the powder feeder dispenser 44 includes powdered matrix material and carbon nanotubes having a discrete length for optimally forming a composite nodal element. As such, the matrix material and carbon nanotubes combine with the fusing agent through a composite nodal element formation sequence implemented by the generation coupling head 40.

10 Those of ordinary skill in the art will readily recognize any combination of carbon nanotubes including single walled and/or multiple walled carbon nanotubes.

In one exemplary embodiment, the generation coupling head 40 controllably disperses discrete fibers, including carbon nanotubes, throughout the matrix. In one exemplary embodiment, the generation coupling head 40 homogeneously disperses  
15 discrete fibers, including carbon nanotubes, throughout the matrix. In one exemplary embodiment, the generation coupling head 40 variably disperses discrete fibers, including carbon nanotubes, throughout the matrix.

In one exemplary embodiment, the multiplicity of fibers may comprise reinforcement fibers for engagement with the matrix. In one exemplary embodiment,  
20 the multiplicity of discrete fibers range in length of between about 10 nanometers to about 500 microns. In one exemplary embodiment, the matrix includes a metal. In one exemplary embodiment, the matrix includes a metal alloy. In one exemplary embodiment, the matrix includes an intermetallic compound. In one exemplary embodiment, the matrix includes a ceramic. In one exemplary embodiment, the matrix  
25 includes a polymer.

To ensure that the formation environment 45 facilitates optimal creation of a free-form structure, the system 30 in one exemplary embodiment includes an environmental control system 50 in operative engagement with the interior of the processing chamber 37. Those of ordinary skill in the art will readily recognize that the system 30 in at least  
30 one exemplary embodiment does not receive an environmental control system 50 and/or a process chamber 37 for the optimal creation of a free-form structure.

In particular, as shown in Figure 3, the environmental control system 50 includes an environmental operating fluid source 51 for supplying an operating fluid to the interior of the processing chamber 37 so as to define the atmosphere included by the formation environment 45. Accordingly, the operating fluid is transferred from the source 51 to the formation environment 45 *via* an inlet 57 in communication with the interior of the processing chamber 37. In one exemplary embodiment, the operating fluid includes, among others, an inert gas, such as argon or nitrogen for introduction into the processing chamber 37.

The environmental control system 50 includes a series of pumps 55 for extracting waste fluid from the formation environment 45. The term waste fluid refers to unwanted fluids resulting from the fabrication of the free-form structure 49. An outlet 59, in communication with the interior of the processing chamber 37, removes waste fluid from the formation environment 45 as driven by the vacuum pump array 55. As shown in Figure 3, the waste fluid is then exhausted from the system 30 *via* a vent assembly 53 in operative engagement with the outlet 59. Moreover, in one exemplary embodiment, a feedback control system 66 coupled to the formation environment 45 is provided by the environmental control system 50 to maintain an optimal formation environment 45 within the processing chamber 37.

The composite formation device 35 further includes an arranger in operative engagement with the composite generator. In one exemplary embodiment, as the composite generator engages with the fusing agent to create a composite nodal element, the arranger positions the forming composite nodal element relative to another to thus define the free form structure 49.

The arranger includes a positioning assembly 60 and a motion controller 61 in operative engagement with the positioning assembly 60. The positioning assembly 60 includes a control system 64. The control system 64 implements program sequences for arranging one node relative to another. The control system 64 further includes program sequences for engaging a fusing agent with a matrix and a multiplicity of carbon nanotube fibers so as to create a composite nodal element.

Specifically, in one exemplary embodiment, a program sequence implemented by the control system 64 includes a composite formation code. The composite

formation code generates a composite node, via the composite generator, by combining a matrix with a multiplicity of fibers formed of carbon nanotubes. Moreover the composite formation code may include a code for homogeneously combining the multiplicity of fibers with the matrix.

5           The control system 64 further includes a structure formation program code for arranging one composite node relative to another via the arranger to define a free-form structure. Moreover, in one exemplary embodiment, the structure formation program code may include a code for arranging one composite node relative to another based on a template.

10           Shown in Figure 3, the positioning assembly 60 further includes an object file storage 62 coupled with the control system 64. Operatively, the object file storage 62 stores a template associated with the free-form structure 49. Moreover, the object file storage 62 contains information associated with the free-form structure 49 based on a computer-readable code. By accessing information stored in the object file storage 62,  
15           the control system 64 moves each one of the nodes according to instructions based on a computer-readable code and/or based on a template.

          With instructions from the control system 64, the motion controller 61 moves each one of the nodes so as to ultimately generate the free-form structure 49. The motion controller 61 includes a worktable 46 having a movable base platform 47. In one  
20           exemplary embodiment, the control system 64 is operatively coupled with the moveable base platform 47 so as to facilitate arrangement of one node relative to another.

          In one exemplary embodiment, the control system 64 is coupled with a motion apparatus 39 provided by the motion controller 61 for positioning the generation coupling head 40 about the processing chamber 37 so as to ultimately facilitate  
25           fabrication of the free-form structure 49. The motion apparatus 39 in one exemplary embodiment comprises a robot coupled to the generation coupling head 40.

          In operation, the control system 64 instructs the motion apparatus 39 to place the generation coupling head 40 relative to the worktable 46. The control system 64 then establishes optimal conditions characteristic of the formation environment 45 for the  
30           fabrication of the free-form structure 49. For one embodiment shown in Figure 3, the generation coupling head 40 combines a fusing agent from the high-powered laser with

a matrix and a multiplicity of carbon nanotubes each provided by the powder feeder dispenser 44.

In particular, the generation coupling head combines the fusing agent, the matrix, and the multiplicity of carbon nanotubes in a single stream 42. Accordingly, Figure 4 shows a perspective view of a system 70 for fabricating of a free form structure 78 from a single stream. The system 70 includes a discharge assembly 74 for dispensing a fusing agent 75. In one exemplary embodiment, the fusing agent 75 comprises a laser beam emission. The system 70 further includes a deposit formation device including a composite generator 72.

In Figure 4, the composite generator 72 engages a matrix and carbon nanotube fibers, collectively shown as stream 76, with the fusing agent 75 so as to create a composite nodal element 79.

As such, in one exemplary embodiment, the composite formation device includes an arranger. The arranger includes a motion apparatus and/or a moveable base platform for positioning one node relative to another to define the free-form structure 78 of Figure 4. Initially, as discussed in greater detail below, a substrate material is ejected from the composite generator 72 for engagement with the fusing agent 75. Accordingly, a substrate 77, and 48 in Figure 3, is cooled and formed atop a worktable. In effect, the substrate acts as a foundation by which each subsequent composite nodal element is deposited on so as to ultimately fabricate the free-form structure 78. Typically, once a free-form structure is completed, the substrate 77 and transition material between the substrate and the desired free form structure is removed from the resulting free form structure prior to use thereof.

Figure 5 refers to a detailed isometric view of a system 80 for fabricating a free-form structure 99. In particular, a composite nodal element 89 is formed by engaging a fusing agent 84 with a matrix 87 and a multiplicity of discrete fibers 88 formed of carbon nanotubes. In one exemplary embodiment, the composite nodal element is characterized as an amorphous or molten weld pool heated by the energy from a laser defining the fusing agent.

The composite nodal element cools and solidifies so as to ultimately define the free-form structure. In one exemplary embodiment, the free-form structure 99 is defined by one layer of composite nodal elements 90 deposited on another 91.

Each successive layer is configured by the system 80 based on information  
5 and/or a template provided by a control system. During the formation of a layer 90, a series of composite nodal elements are generated adjacent to one another along the travel direction of the fusing agent, as shown in Figure 5 as reference arrow "t". In one exemplary embodiment, to ensure material and structural continuity, the fusing agent provides energy so as to partially melt composite nodal elements adjacent to the  
10 composite nodal element being formed thereby integrating the newly formed composite nodal element with the other composite nodal elements.

Referring to the operation of system 80, a layer of substrate material 95 is initially deposited as a foundation by which the free-form structure 99 is subsequently deposited thereon. Typically, the amorphous or viscous material state of the newly  
15 formed substrate material results in the creation of a transitional layer 93. During formation of the transitional layer 93, stray amorphous substrate material combines, *via* the system 90, with the desired composite material defining the free-form structure 99. Ultimately, after completion of fabrication of the free-form structure 99 the transition layer 93 and substrate layer 95 are removed from the free-form structure 99.

20 As shown in Figure 5, the deposition of each successive composite nodal element layer, such as for example layers 90, 91, is associated with the movement of a composite formation device 82 while receiving a fusing agent 84 along a travel direction, "t". As shown in Figures 4 and 5, in one exemplary embodiment, the matrix material 87, in a powdered form, is mixed with discrete carbon nanotube fibers 88 to form a single  
25 stream. As the stream receives energy from the fusing agent 84, a composite nodal element 89 is created. For one embodiment of Figure 5, the fibers of carbon nanotubes are of a predetermined length "d", as indicated in Figure 5, for the optimal formation of a composite nodal element. In one exemplary embodiment, the multiplicity of discrete fibers range in length of between about 10 nanometers to about 500 microns.

30 For the exemplary embodiment of Figure 6, a free-form structure 120 is fabricated by a system 100. Although including similar aspects as that of the system 30

of Figure 3, the system 100 of Figure 6 provides a different rapid manufacturing process for fabricating a free-form structure. Generally, system 100 differs in that matrix and carbon nanotube materials are combined with a fusing agent in a different manner than that of the system 30 of Figure 3.

5 As distinguished from the generation coupling head 40 and movement applied thereto, in part, by the motion apparatus 39 of Figure 3, the system 100 of Figure 6 includes a raw material container 117 containing a powder bed 122. The powder bed 122 includes a matrix powder and a multiplicity of fibers formed of carbon nanotubes dispersed throughout the matrix powder. Operatively, a discharge assembly 125, such  
10 as a high-powered laser for example, dispenses a fusing agent from a focus head 115 so as to subject discrete portions of the powder bed 122 to a fusing agent, such as a laser beam. Accordingly, the free-form structure 120 is created from fused sections within the powder bed 122. It should also be added that a worktable 119 may be provided to position the free-form structure 120 during fabrication.

15 However, similar to the system 130 of Figure 3, the system 100 of Figure 6 includes an environmental control system 130 including an operator fluid source 131, a vent assembly 133, a pump system 135, and a feedback 146. In addition, the system 100 includes a control system 144 and an object file storage 142 coupled to the control system 144, both of which are included by the positioning array 140. In one exemplary  
20 embodiment, the discharge assembly 125 includes a high energy density source. In one exemplary embodiment, the discharge assembly 125 includes a high-powered laser. Moreover, the system 100 includes a processing chamber 111 for enclosing a formation environment 113.

Figure 7 refers to the free-form fabrication sequence 200 executed by the system  
25 30 of Figure 3. The free-form fabrication sequence 200 illustrates one exemplary embodiment for fabricating a free-form structure defined by an array of composite nodal elements that include a multiplicity of carbon nanotubes dispersed throughout a matrix. In one exemplary embodiment, the multiplying of carbon nanotubes are controllably dispersed throughout a matrix. In one exemplary embodiment, the  
30 multiplying of carbon nanotubes are homogeneously dispersed throughout a matrix. Those of ordinary skill in the art will readily recognize other free-form fabrication



sequences so long as a resulting free-form structure includes composite material based on carbon nanotubes dispersed throughout a matrix.

Referring to Figure 7, the free-form fabrication sequence 200 includes a system start-up routine 210, a chamber preparation routine 220, a robot initiation routine 230, and a deposition routine 240. The system start-up routine 210 includes supplying the system 30 with matrix and nanotube raw materials as per step 211. In step 213, the high-powered laser 43 and the generation coupling head 40 of Figure 3 are activated. In step 215, the vacuum pump array 55 of the environmental control system 50 is activated.

The chamber preparation routine 220 in step 221 includes optimally positioning the motion controller 61 for processing operations. In step 223, a vacuum is established within the processing chamber 37. In step 225, an operating fluid is applied to the formation environment 45.

The robot initiation routine 230 of Figure 7 may include accessing the object file storage 62 and retrieving an object file therefrom. The object file includes, among others, information associated with size, dimensioning, tolerancing, and material composition of the desired free-form structure. In step 233, through instructions in a machine-readable code, the desired object is partitioned so as to correspond with the control paths executed by the arranger. In step 235, the control system 64 sends the partitioned object file to the generation coupling head 40 and to the motion controller 61, including the motion apparatus 39, and the moveable base platform 47. Based on the information received from the control system 64, the motion controller 61 is activated in step 237.

The deposition routine 240 includes initiating the powder feeder dispenser 44 in step 241 and engaging dispensing of a fusing agent in step 243. Based on information received by the control system 64, the motion controller 61, including the motion apparatus 39, traces the control path for the deposition and arrangement of composite nodal elements in step 244. In step 245, the deposition continues so as to create a solid part or free-form structure.

Referring to Figure 8, the composite nodal element formation sequence 300 generally includes an initialization routine 305 and a formation routine 330 operatively

linked with the initialization routine 305. Depending on the type of rapid manufacturing technique and/or system used, the initialization routines 305 vary. Although those of ordinary skill in the art will readily recognize other suitable initialization routines based on the type of rapid fabrication processes and/or systems used to create composite structures that include carbon nanotubes, Figure 8 shows two initialization routines. Specifically, in one exemplary embodiment, Figure 8 includes an initialization routine 310 for system 30 of Figure 3. Figure 8, in one exemplary embodiment, further includes an initialization routine 320 for system 100 of Figure 6.

Referring to the initialization routine 310, matrix material in powder form is loaded into one dispenser system of the powder feeder 44 of Figure 3. Similarly, the carbon nanotube fibers are loaded into another dispenser system of the powder feeder 44, apart from the dispenser system in step 311. As such, in step 315, powders are fed into a stream of operating fluid, such as an inert gas. Moreover, in step 315, the matrix material and carbon nanotube material are combined and mixed in the flowing stream of operating fluid.

Alternatively, for the initialization routine 320 matrix material is mixed with carbon nanotubes in step 321 prior to being fed into an operating fluid stream. In other words, whereas the initialization routine 310 provides for an *in situ* combination of matrix material and carbon nanotubes prior to introduction into an operating fluid stream, the initialization routine 320 provides for an *ex situ* combination of matrix material and carbon nanotubes prior to introduction with an operating fluid stream. Accordingly, the mixture of matrix material and carbon nanotubes from step 321 are loaded into a powder feeder dispenser 44 in step 323. In step 325, the mixture of matrix material and carbon nanotubes is fed into a flowing stream of operating fluid.

For the formation routine 330, once a powder-gas mixture is established *via* the initialization routine 305, the powder-gas mixture is carried into the processing chamber 37 through feed-tubes. In step 334, for the system 30 of Figure 3, the generation coupling head 40 splits the powder-gas mixture into a plurality of streams. In step 336 each stream is carried to a nozzle provided by the generation coupling head 40.

As illustrated in Figure 4, each stream of powder-gas mixture exits a respective nozzle and, for a location determined by the control system 64, combines with a fusing agent such as a laser beam emission. The combination of exiting powder combined with the fusing agent in step 338 results in the formation of a molten composite nodal element. Accordingly, in step 340 the resulting composite nodal element solidifies so as to define a free-form structure, as illustrated for example in Figure 5.

Although the present invention has been described in detail, it should be understood that various changes, substitutions, and alterations can be made hereto without departing from the spirit and scope of the invention as defined by the appended claims that follow.

**WHAT IS CLAIMED IS:**

1. A system for fabricating a free form structure, the system comprising:  
a discharge assembly for dispensing a fusing agent;  
a composite formation device;  
5 the composite formation device comprising  
a composite generator, the composite generator engaging with the fusing  
agent so as to create a composite nodal element;  
the composite nodal element containing a matrix and a multiplicity of  
fibers formed of carbon nanotubes dispersed throughout the matrix; and  
10 an arranger in operative engagement with the composite generator;  
the arranger positioning one node relative to another to define the free  
form structure.
2. The system according to Claim 1 wherein the composite formation device  
15 combines the fusing agent with the matrix and the multiplicity of fibers to form the  
composite nodal element.
3. The system according to Claim 1 wherein the fusing agent comprises a  
high energy density emission.  
20
4. The system according to Claim 1 wherein the arranger includes a  
positioning assembly.
5. The system according to Claim 4 wherein the positioning assembly stores  
25 a template associated with the free form structure.
6. The system according to Claim 5 wherein the positioning assembly moves  
each one of the nodes according to the template.
- 30 7. The system according to Claim 4 wherein the positioning assembly moves  
each one of the nodes according to instructions based on a computer readable code.

8. The system according to Claim 1 wherein the multiplicity of fibers are controllably dispersed throughout the matrix.

5 9. The system according to Claim 1 wherein the multiplicity of fibers comprise reinforcement fibers.

10. The system according to Claim 1 wherein the multiplicity of fibers range in length of between about 10 nanometers to about 500 microns.

10

11. The system according to Claim 1 wherein the matrix includes a metal.

12. The system according to Claim 1 wherein the matrix includes a metal alloy.

15

13. The system according to Claim 1 wherein the matrix includes an intermetallic compound.

14. The system according to Claim 1 wherein the matrix includes a ceramic.

20

15. The system according to Claim 1 wherein the matrix includes a polymer.

16. A free form composite structure comprising:

a matrix; and

25

a multiplicity of reinforcement elements formed of carbon nanotubes;

the multiplicity of reinforcement elements dispersed throughout the matrix.

17. The free form structure according to Claim 16 wherein the multiplicity of reinforcement elements are homogeneously dispersed throughout the matrix.

30

18. The free form structure according to Claim 16 wherein the reinforcement elements range in length of between about 10 nanometers and 500 microns.

19. A program product executed by a computer readable code for fabricating  
5 a free form structure via a fabrication system, the fabrication system including a composite generator and an arranger, the program product comprising:

a composite formation program code for generating a composite node via the composite generator by combining a matrix and a multiplicity of fibers formed of carbon nanotubes; and

10 a structure formation program code for arranging one composite node relative to another via the arranger to define a free form structure.

20. The program according to Claim 19 wherein the composite formation program code includes code for homogeneously combining the multiplicity of fibers  
15 with the matrix.

21. The program according to Claim 19 wherein the structure formation program code includes code for arranging one composite node relative to another based on a template.

20

22. A method for fabricating a free form structure via a composite formation device, the method including the steps of:

combining a matrix and a multiplicity of fibers formed of carbon nanotubes;

generating a plurality of composite nodes from the combination of the matrix

25 and the multiplicity of fibers; and

arranging one composite node relative to another.

23. The method according to Claim 22 wherein the step of combining a matrix and a multiplicity of fibers comprises the step of controllably dispersing the multiplicity  
30 of fibers throughout the matrix.

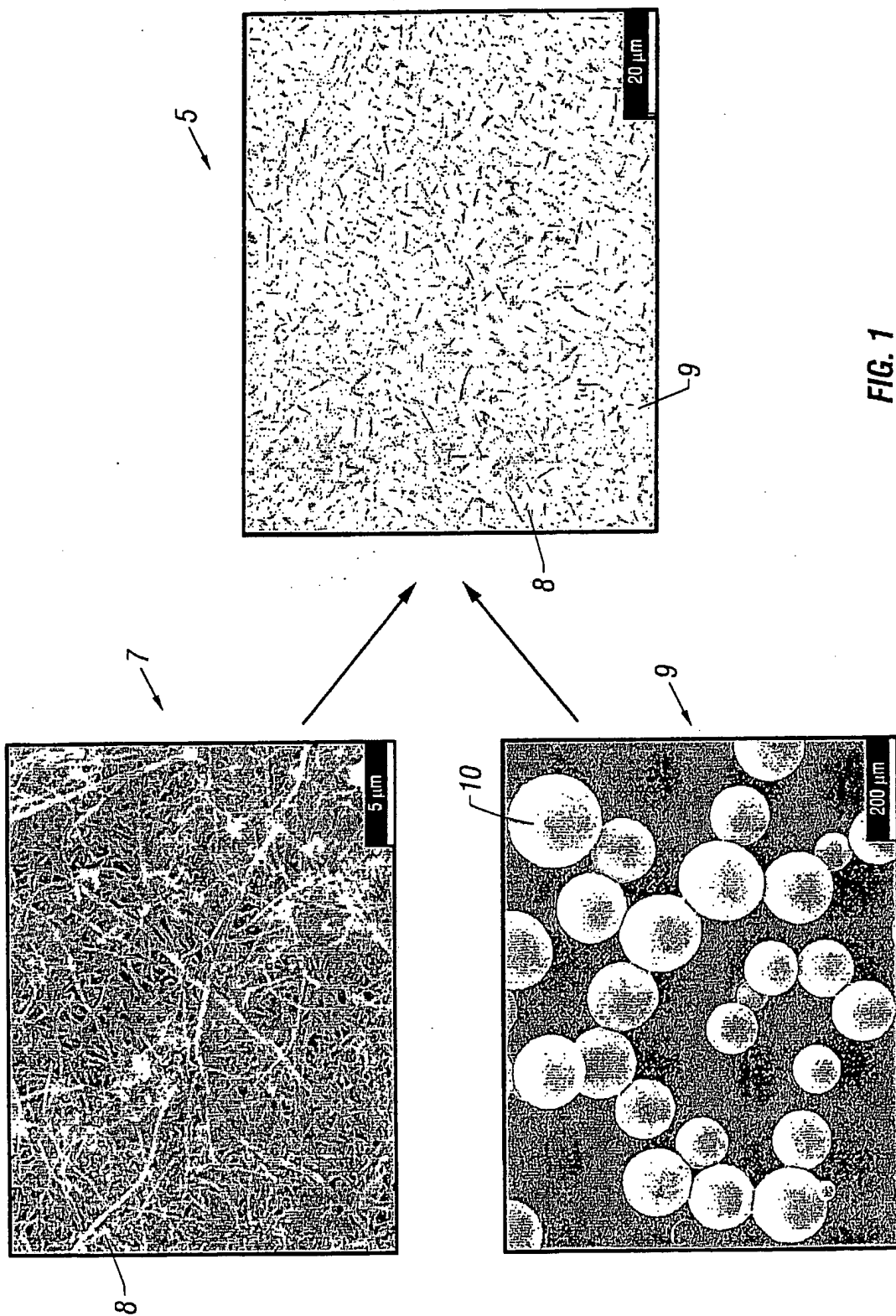
24. The method according to Claim 22 wherein the step of combining a matrix and a multiplicity of fibers comprises the step of homogeneously dispersing the multiplicity of fibers throughout the matrix.

5        25. The method according to Claim 22 wherein the step of combining a matrix and a multiplicity of fibers comprises the step of variability dispersing the multiplicity of fibers throughout the matrix.

10       26. The method according to Claim 22 wherein the step combining a matrix and a multiplicity of fibers comprises the step of applying a fusing agent to the matrix and the multiplicity of fibers.

15       27. The method according to Claim 22 wherein the step of arranging one composite node relative to another comprises the step of moving each one of the nodes based on a template.

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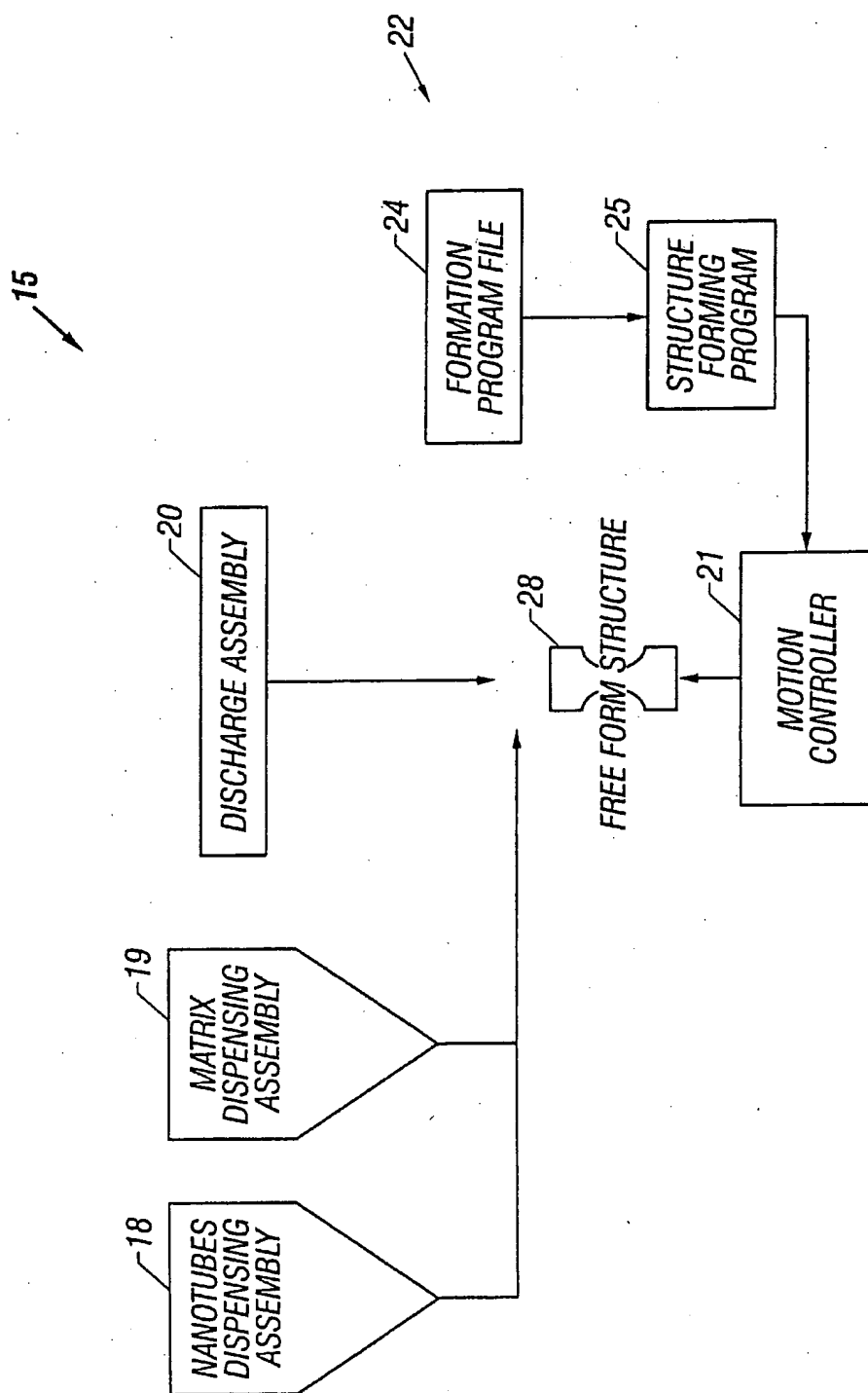


FIG. 2

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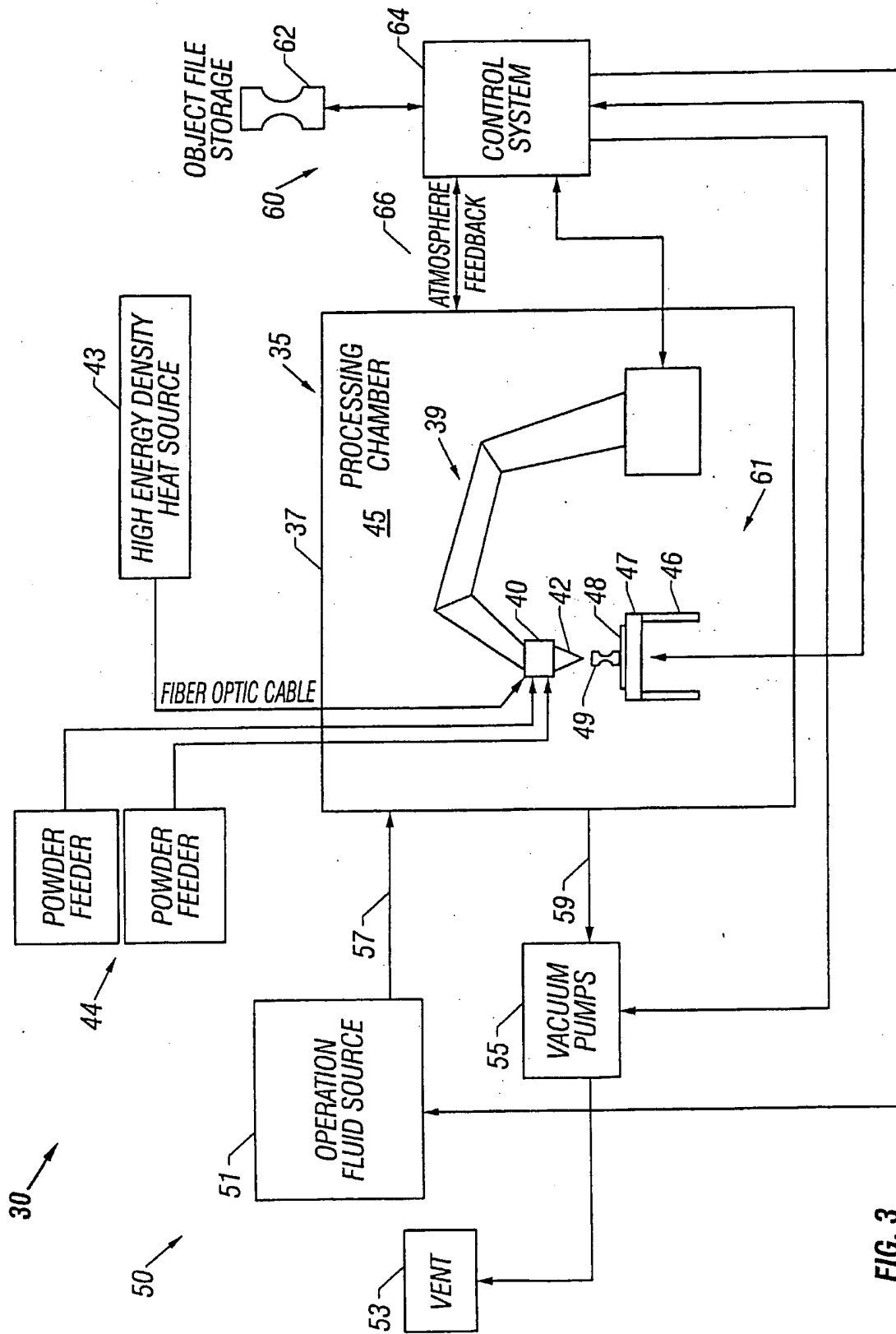


FIG. 3

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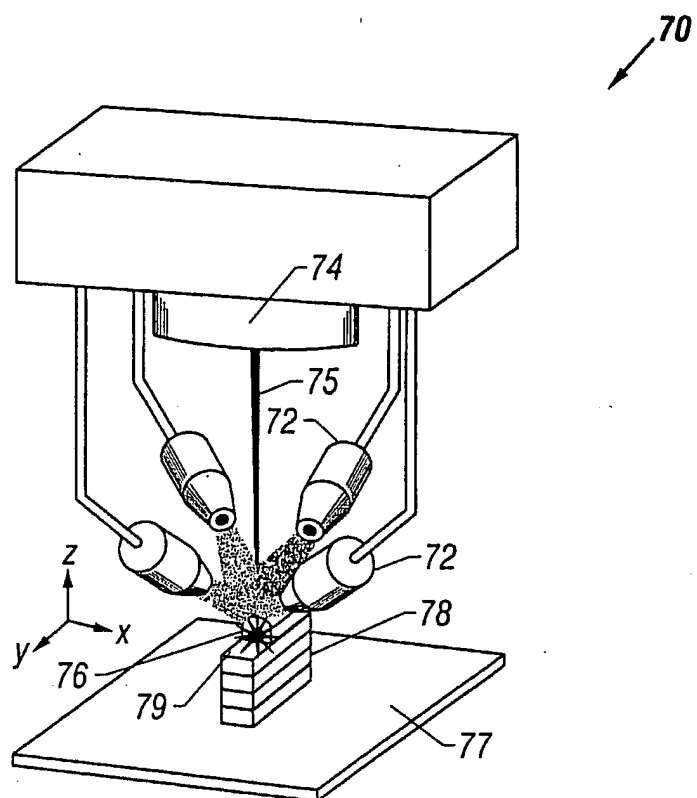


FIG. 4

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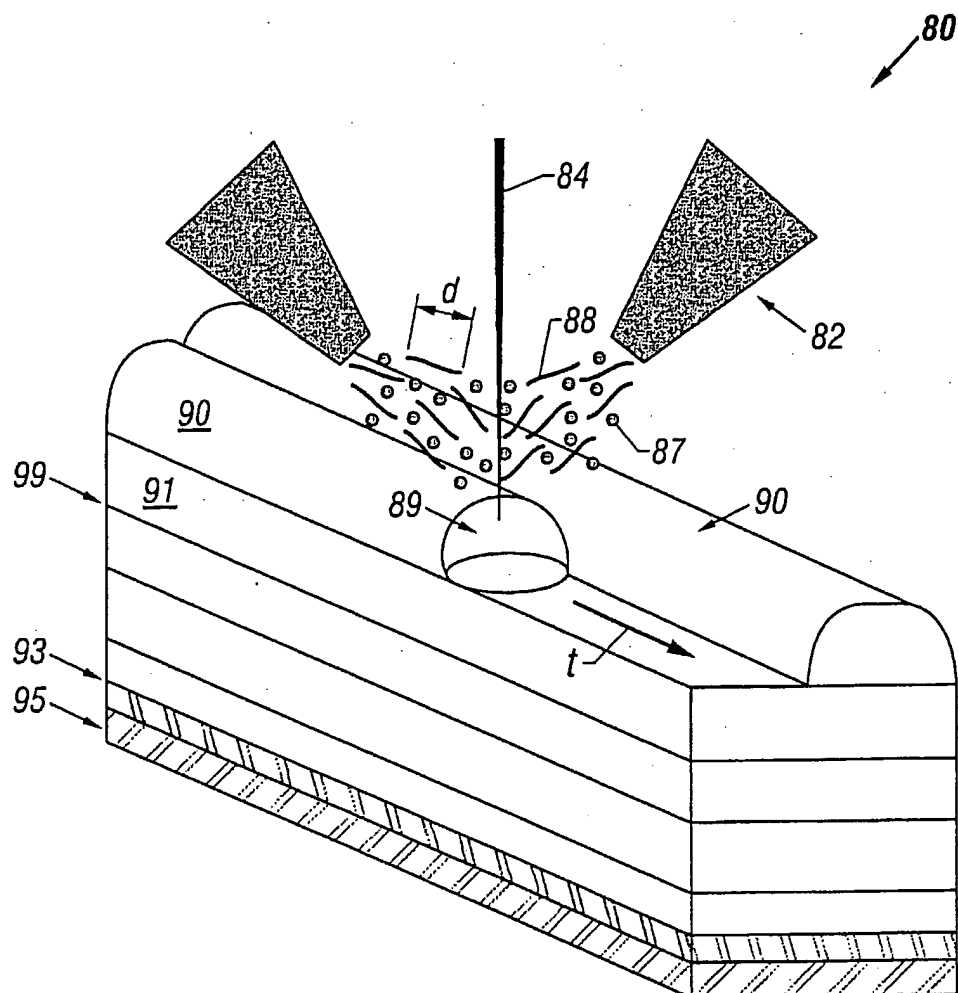
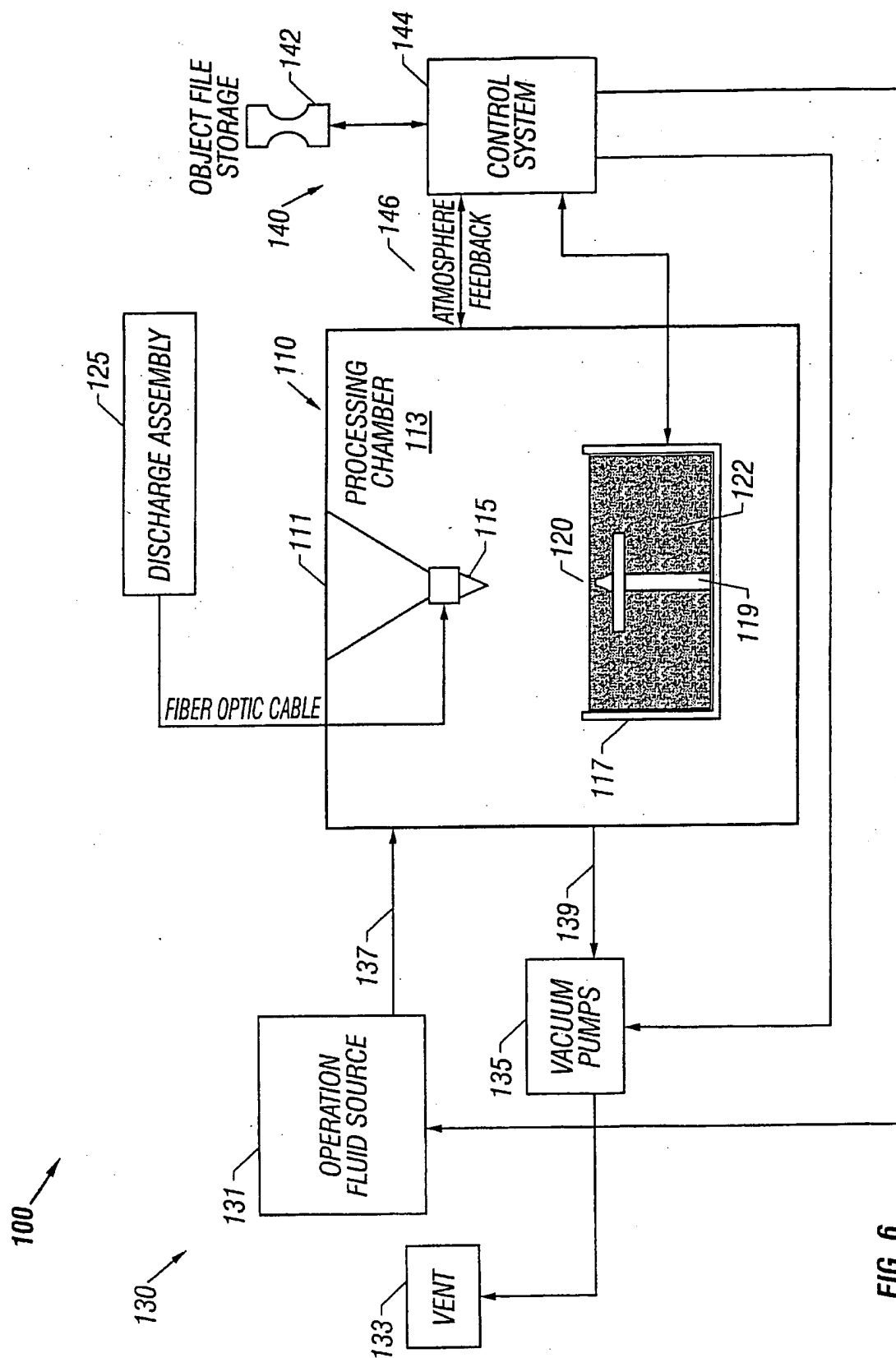


FIG. 5

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**FIG. 6**

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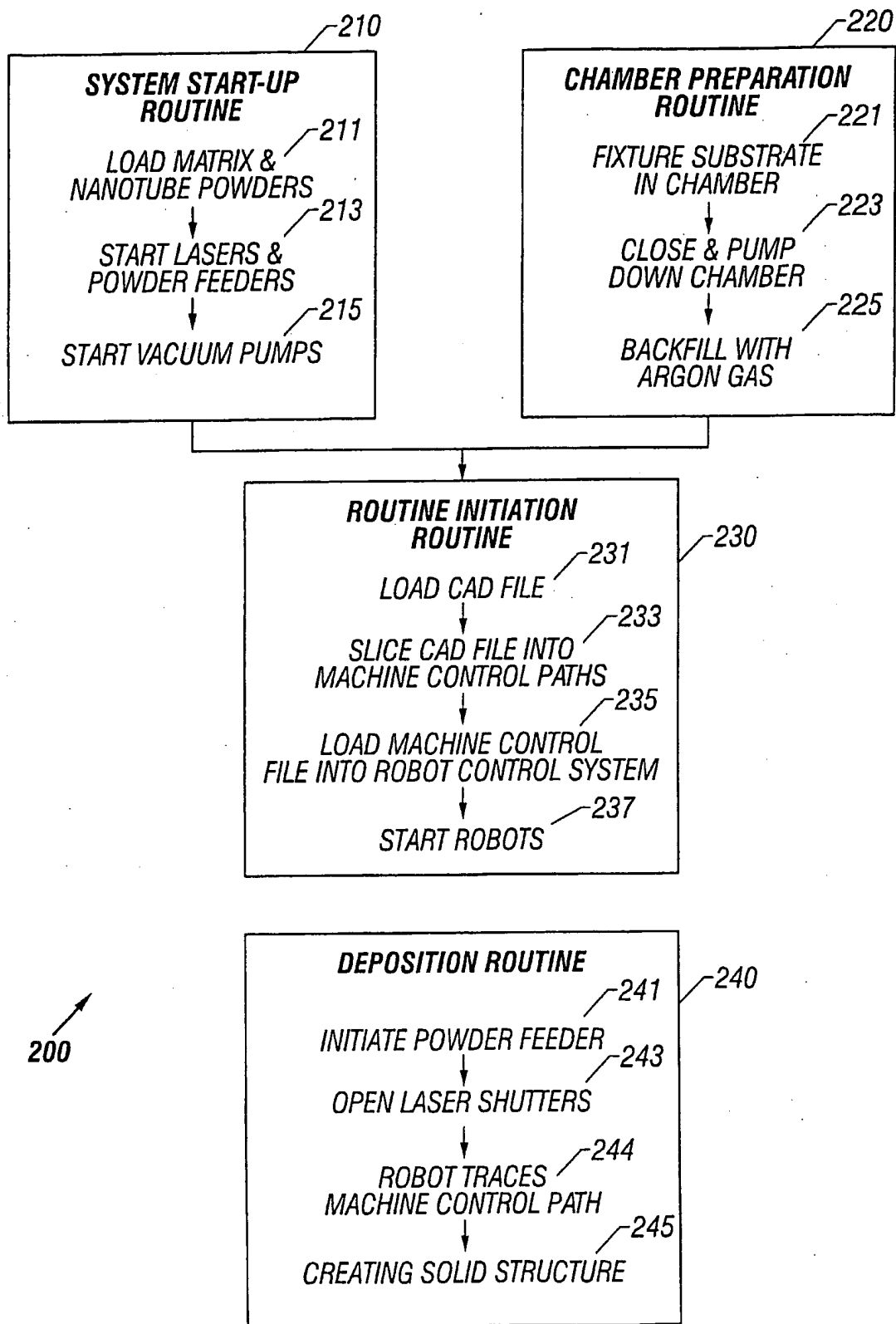


FIG. 7

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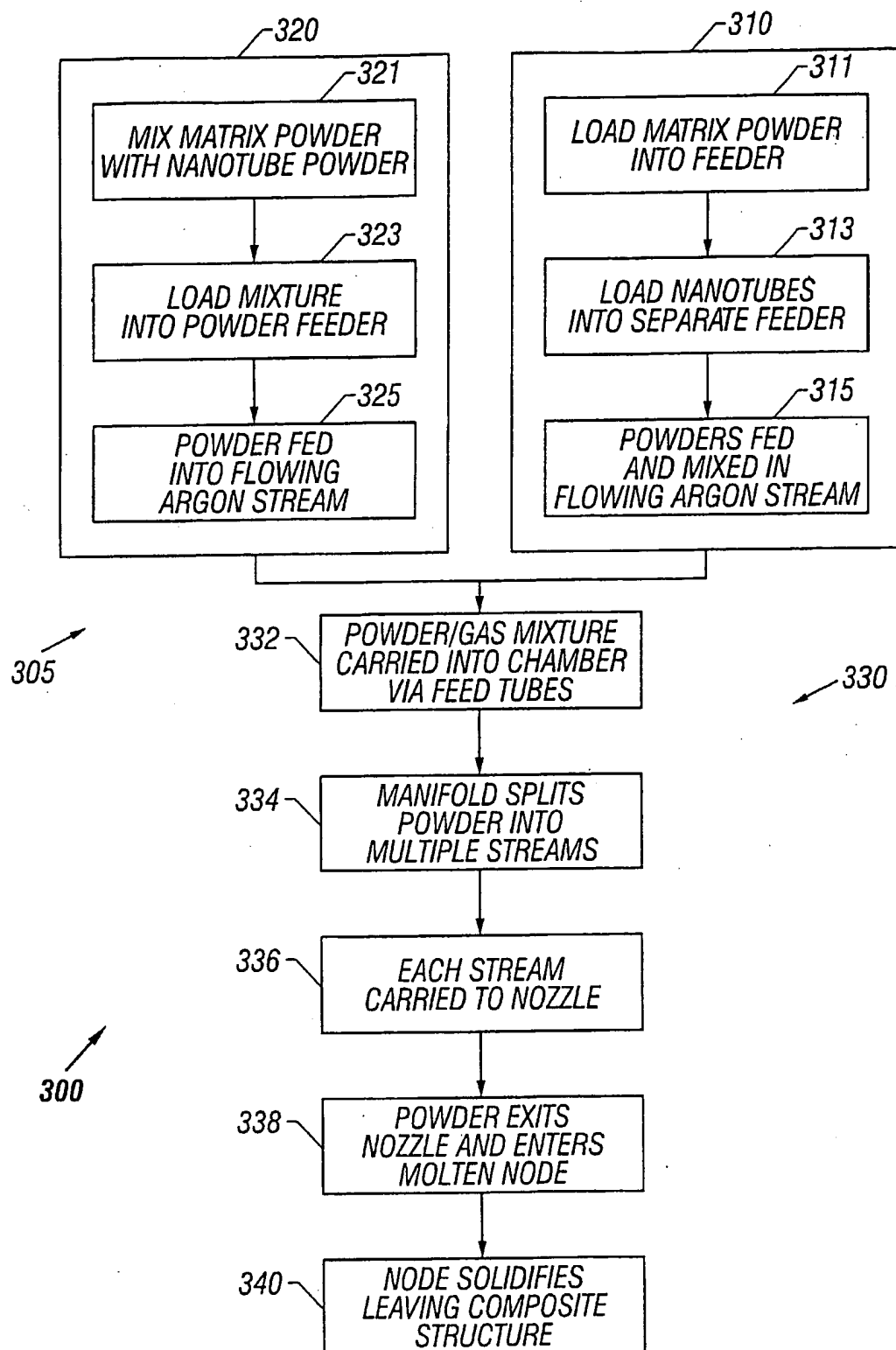


FIG. 8

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- Published:  
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- (88) Date of publication of the international search report:  
16 January 2003
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: RAPID MANUFACTURING OF CARBON NANOTUBE COMPOSITE STRUCTURES

(57) Abstract: A system for fabricating a free form structure of a composite material including carbon nanotubes. The system includes a discharge assembly and a composite formation device operatively linked with the discharge assembly. The discharge assembly dispenses a fusing agent such as for example a high energy density emission, a laser emission or a particle beam emission. The composite formation device includes a composite generator and an arranger in operative engagement with a composite generator. The composite generator engages with the fusing agent so as to create a composite nodal element. The composite nodal element includes a matrix and a multiplicity of fibers formed of carbon nanotubes dispersed throughout the matrix. The arranger positions one node relative to another to define the free form structure.

WO 02/042204 A3



## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/51150

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 C01B31/02 B29C70/12 C22C1/09

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B B29C C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, INSPEC

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	EP 1 054 036 A (FINA RESEARCH) 22 November 2000 (2000-11-22) paragraphs '0006!', '0007!', '0009!', '0015!' ---	16-18
X	EP 1 022 764 A (LUCENT TECHNOLOGIES INC) 26 July 2000 (2000-07-26)	16-18
A	paragraphs '0022!-'0025!', '0030!', '0031!' ---	22-27
X	FLAHAUT E ET AL: "CARBON NANOTUBE-METAL-OXIDE NANOCOMPOSITES: MICROSTRUCTURE, ELECTRICAL CONDUCTIVITY AND MECHANICAL PROPERTIES" ACTA MATERIALIA, ELSEVIER, OXFORD, GB, vol. 48, no. 14, 4 September 2000 (2000-09-04), pages 3803-3812, XP001005688 ISSN: 1359-6454 page 1 -page 2 --- -/-	16-18

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

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Date of the actual completion of the international search

11 September 2002

Date of mailing of the international search report

20/09/2002

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/51150

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 02 18296 A (AJAYAN PULICKEL M ;CHANG SEKYUNG (US); DOREMUS ROBERT H (US); RENS) 7 March 2002 (2002-03-07) claims 1-4,7,12,13; example 2 ---	16-18, 22-26
P,A	US 6 144 008 A (RABINOVICH JOSHUA E) 7 November 2000 (2000-11-07) the whole document ---	22-27
X	US 6 122 884 A (TALWAR RAJESH) 26 September 2000 (2000-09-26) column 4, line 62 -column 6, line 42 ---	22-27
A	US 5 147 587 A (MARCUS HARRIS L ET AL) 15 September 1992 (1992-09-15) column 3, line 47 -column 5, line 24 -----	22-27

## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-15, 19-21

Present claims 1-15, 19-21 relate to an extremely large number of possible apparatus and products. In fact, the claims contain so many options, variables, possible permutations and provisos that a lack of clarity (and/or conciseness) within the meaning of Article 6 PCT arises to such an extent as to render a meaningful search of the claims impossible. Consequently, the search has been carried out for those parts of the application which do appear to be clear (and/or concise), namely claims 16-18 and 22-27 relating to a composite material and to a method for preparing a composite material.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 01/51150

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1-15, 19-21  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/51150

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1054036	A	22-11-2000	EP 1054036 A1	22-11-2000
			AU 4565900 A	05-12-2000
			WO 0069958 A1	23-11-2000
			EP 1181331 A1	27-02-2002
			US 6331265 B1	18-12-2001
EP 1022764	A	26-07-2000	US 6250984 B1	26-06-2001
			AU 6447399 A	27-07-2000
			EP 1022764 A1	26-07-2000
			JP 2000223004 A	11-08-2000
WO 0218296	A	07-03-2002	US 6420293 B1	16-07-2002
			AU 8340301 A	13-03-2002
			WO 0218296 A1	07-03-2002
US 6144008	A	07-11-2000	NONE	
US 6122884	A	26-09-2000	US 6064031 A	16-05-2000
US 5147587	A	15-09-1992	US 4944817 A	31-07-1990
			US 4863538 A	05-09-1989
			AT 155381 T	15-08-1997
			AT 160960 T	15-12-1997
			AU 643700 B2	25-11-1993
			AU 6206590 A	14-03-1991
			CA 2024592 A1	06-03-1991
			DE 9018138 U1	08-02-1996
			DE 69031061 D1	21-08-1997
			DE 69031061 T2	30-10-1997
			DE 69031808 D1	22-01-1998
			DE 69031808 T2	02-04-1998
			DK 714725 T3	10-08-1998
			EP 0416852 A2	13-03-1991
			EP 0714725 A1	05-06-1996
			ES 2104588 T3	16-10-1997
			ES 2111408 T3	01-03-1998
			JP 3183530 A	09-08-1991
			US 5431967 A	11-07-1995
			US 5382308 A	17-01-1995
			US 5156697 A	20-10-1992
			US 5182170 A	26-01-1993
			US 5284695 A	08-02-1994
			US 5296062 A	22-03-1994
			AT 116179 T	15-01-1995
			AT 138294 T	15-06-1996
			AT 138293 T	15-06-1996
			AU 603412 B2	15-11-1990
			AU 1046688 A	06-05-1988
			AU 659289 B2	11-05-1995
			AU 3524193 A	13-05-1993
			AU 632195 B2	17-12-1992
			AU 6834690 A	14-03-1991
			BG 47343 A3	15-06-1990
			BR 8707510 A	21-02-1989
			CA 1284868 A1	18-06-1991
			DE 3750931 D1	09-02-1995
			DE 3750931 T2	11-05-1995
			DE 3751818 D1	27-06-1996

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/51150

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5147587 A		DE 3751818 T2	26-09-1996
		DE 3751819 D1	27-06-1996
		DE 3751819 T2	26-09-1996
		DE 8718128 U1	01-02-1996
		DE 287657 T1	18-08-1994
		DK 329888 A	15-08-1988
		EP 0287657 A1	26-10-1988
		EP 0542729 A2	19-05-1993
		EP 0538244 A2	21-04-1993
		FI 882881 A ,B,	16-06-1988
		HK 194796 A	01-11-1996